PATENT SPECIFICATION (11) 1 513 550

1 513 550

(21) Application No. 18770/75 (22) Filed 5 May 1975
(23) Complete Specification filed 3 May 1976
(44) Complete Specification published 7 June 1978
(51) INT CL² C11D 10/02 (C11D 10/02, 1/00, 3/04, 3/33)
(52) Index at acceptance
C5D 6A5C 6A6 6B11C 6B12B1 6B12F2 6B12G1 6B12G2A 6B1 6B2 6C8

(72) Inventor JEFFREY DALE HAMPSON

(19)

(54) HARD SURFACE CLEANING COMPOSITIONS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London EC4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

One of the prerequisites of a satisfactory hard surface cleaning composition is that it should have a good foam performance, i.e. the composition should produce a uniform, stable foam.

For the purposes of the present invention, a hard surface cleaning composition is a cleaning composition to be used for cleaning of dishes, pots, pans, tiles, floors i.e. hard substrates. In the specification the hard surface cleaning composition is typically exemplified by dishwashing compositions, but is not limited thereto.

The production of a uniform, stable foam is required for dishwashing compositions for use in manual dishwashing operations, where it is a measure for the effectiveness of the dishwashing compositions.

Many dishwashing formulations yield an acceptable foam behaviour in either hard or soft water; a formulation for use in hard water is frequently not suitable for use in soft water, and the reverse is also often true.

The present invention provides a hard surface cleaning composition which is suitable for use in both hard and soft water. Its foam behaviour in both hard and soft water is significantly improved, thus providing a formulation of which the foam behaviour is relatively independent of the water from which the washing-up liquor is produced.

Essentially this is achieved by incorporating in a dishwashing composition an organic sequestering agent which will be hereinafter defined, and a magnesium salt which will also be defined hereafter, the dishwashing composition further preferably comprising particular types of active detergent materials, as described in more detail hereafter.

The organic sequestering agents to be used in the present invention have a difference in pK values for calcium and magnesium of at least 0.5, and preferably 1 or more. Furthermore, they have a pK value for calcium of at least 3.

Suitable examples of organic sequestering agents to be used in the present invention are

	pK ++ Ca	pK ++ Mg	Δ pK
nitrilotriacetic acid (NTA)	6.5	5.5	1.0
dipicolinic acid (DPA)	4.6	2.4	2.2
ethylenediaminetetra acetic acid (EDTA)	10.6	8.7	1.9
hydroxyethyl-ethylenediaminetri-acetic acid (Hydroxy-EDTA)	8.0	5.2	2.8
1,2 diaminecyclohexane-N,N'-tetra-acetic acid (DCHTA)	12.5	10.3	2.2
2-sulfoaniline diacetic acid (SADA)	4.57	2.68	1.89
2-aminobenzoic acid, N,N diacetic acid (ABDA)	5.06	3.91	1.15
N-aceto amidoimino diacetic acid (AADA)	3.96	2.47	1.49
N-methoxyethylimino diacetic acid (MEDA)	4.53	3.31	1.22
N-hydroxyethylimino diacetic acid (HEDA)	4.63	3.44	1.19
trimethylenediaminetetra acetic acid (TMETA)	7.12	6.02	1.10
tetramethylenediaminetetra acetic acid (TeMETA)	5.05	3.44	1.61
1,2-bis[2-[di(carboxymethyl)amino] ethoxy]ethane (DCMA)	11.0	5.2	5.80
N-hydroxyethyl-N,N',N",N"-di ethylene-triaminetetra acetic acid (HEDETA)	8.4	6.9	1.50

Although in the above enumeration the acids are mentioned, it is to be understood that the alkali metal salts, such as sodium salts, as well as ammonium and substituted ammonium salts of these acids are also included within the scope of the present invention.

The choice of an organic sequestering agent according to the present invention within the scope of the above definition is further governed by the pH of the dishwashing composition in solution: it is clear that at pH-values below the pK-values of the organic sequestering agent the complexing power is considerably reduced, so one would select an organic sequestrant with a pK value below the pH obtained in use.

For dishwashing purposes furthermore, where the pH of the system is 9 or less, the organic sequestrant should have a pK for calcium of not greater than 8, preferably below 7.5. For other hard surface cleaning purposes, such as floor cleaning, cleaning of tiles and sinks, the pK for calcium can be higher.

For dishwashing compositions the preferred organic sequestrants are NTA, dipicolinic acid, and hydroxyethylimino diacetic acid, and for other hard surface cleaning purposes hydroxy EDTA, DCHTA, and EDTA may suitably be used.

The amount of the organic sequestering agent (or mixtures of sequestering agents) is also relatively critical; in general there should be present at least 3% by weight of the total compositon: lower amounts, e.g. in the order of 1% or less do not provide the desired foam behaviour. The maximum amount of the organic sequestering agent is 60% by weight of the total composition. Preferably the amount is from 8 to 40%. The magnesium salts which are used in the present invention are inorganic and/or organic magnesium salts, having a solubility product of at least 5×10^{-5}. Furthermore, for dishwashing purposes, the magnesium salt should not buffer at a pH above 9.

Suitable examples of inorganic magnesium salts are magnesium sulphate, chloride, bromide, iodide and nitrate, and suitable examples of organic magnesium salts are magnesium citrate and tartrate, and the magnesium salt(s) of EDTA.

The amount of magnesium salts to be used in the present invention varies from 0.5—30%, and preferably ranges from 2 to 15% by weight.

The organic sequestrants of the present invention are particularly useful in compositions which comprise calcium-sensitive active detergent materials. The latter are more or less readily precipitated from solutions by calcium ions present as the water hardness salts in e.g. natural waters, which results in loss of performance in terms of cleaning, wetting and foam stability. Examples of such calcium-sensitive active detergent materials are (C_{10}—C_{18} alkyl)benzene sulphonates, C_{12}—C_{18} sec. alkane sulphonates, C_{10}—C_{20} sec. alkyl sulphates, C_{10}—C_{18} primary alkyl sulphates, sulpho succinates and their mono and di C_6C_{12} alkyl esters, C_{12}—C_{18} fatty acid soaps, and mixtures thereof. These active materials include their alkali metal, ammonium and substituted ammonium salts. Preferably the sodium salts are used. The calcium-sensitive active detergent materials should have a solubility product of less than 6×10^{-11}, preferably less than 3×10^{-11}. These calcium-sensitive active materials may be used in conjunction with other, less calcium-sensitive active materials such as C_{10}—C_{18} alkyl sulphates containing 1—10 moles of ethylene oxide, nonionic detergent-active materials such as condensation products of ethylene oxide with primary or secondary C_{10}—C_{18} alcohols, C_{10}—C_{18} fatty acids and fatty amides and C_8—C_{18} alkylphenols; furthermore zwitterionic detergent actives such as sulphobetaines; alkylaminocarboxylic acids; and tertiary amine oxides. In general, when using the calcium-sensitive detergent actives in conjunction with less calcium-sensitive detergent actives, the former constitute at least 50% by weight of the mixture. The total amount of active detergent material ranges from 1—55% by weight. For dishwashing purposes the amount is preferably 15—45% by weight, and for other hard surface cleaning compositions it is preferably 2—25% by weight.

The composition of the invention can be formulated into particulate, solid, pasty or liquid detergent formulations by methods well-known in the art. The balance of the composition, if any, may comprise the usual detergent adjuvants such as inorganic salts such as alkali metal sulphates, carbonates, orthophosphates and silicates, furthermore lather boosters such as fatty acid mono- and dialkylolamides, hydrotropes such as ureas, ethanol, sodium xylene- and toluene sulphonates, enzymes, germicides, perfumes, colouring materials, opacifiers, corrosion inhibitors, anti-tarnishing agents and china-pattern damage inhibitors.

The inventions will now further be illustrated by the following Examples.

In these Examples the foam stability was measured by diluting the product in water with the indicated hardness, to the indicated product concentration, after which foam was generated by agitation. Increments of soil were then added to this solution at 45°C with further agitation until the foam collapsed. The results were expressed as the number of soil increments to destroy the foam. Percentages are by weight, unless indicated otherwise. Examples 1—3 are not according to the invention, but serve to illustrate more clearly the invention as exemplified in Examples 4—6.

Example 1.

A composition comprising 27% of sodium C_{11}—C_{13} alkylbenzene sulphonate and 3% sodium sulphate was dosed in water of varying hardness to a product concentration of 0.15%. The following foam stability results were obtained:

Water hardness (°FH, calcium)	Numbers of soil increments to destroy foam
0	10
1	30
2	44
4	28
10	10

These results show that the performance significantly decreases with increasing water hardness.

Example 2.

A composition containing 27% sodium C_{11-13} alkylbenzene sulphonate, 15% sodium tropoly phosphate, and 58% sodium sulphate was diluted with water of varying hardness to a product concentration of 0.15%, and the results of the foam stability tests were as follows:

Water hardness (°FH)	Number of soil increments to destroy foam
20	42
10	30
4	8
1	4

These results show that the performance significantly decrease with decreasing water hardness, using a conventional builder salt such as sodium tripoly phosphate.

Example 3.

Using the same formulation of Example 2, in which however 4% of the sodium sulphate was replaced by 4% magnesium sulphate, the following results were obtained:

Water hardness (°FH)	Number of soil increments to destroy foam
20	40
10	42
4	32
1	8

These results show that the performance in soft water is improved, but in very soft water the performance drops off significantly.

Example 4.

A composition containing 27% sodium C_{11-13} alkylbenzene sulphonate, 20% trisodium nitrilotriacetate, 10% magnesium sulphate and 43% sodium sulphate was diluted with water of varying hardness to a product concentration of 0.15% (pH = 8.1). The foam stability test yielded the following results:

Water hardness (°FH)	Number of soil increments to destroy foam
20	40
10	41
4	39
1	30

The following composition: 27% sodium C_{11-13} alkylbenzene sulphonate, 14% sodium salt of dipicolinic acid, 10% magnesium sulphate and 49% sodium sulphate, when used under the same conditions as above, gave the following results:

Water hardness (°FH)	Number of soil increments to destroy foam
5	50
10	50
24	40

These results show that a significantly improved performance is obtained over a wide range of water hardness conditions, i.e. in both soft and hard water.

Example 5.

Using a liquid formulation containing:
27% Sodium C_{11}—C_{13} alkylbenzene sulphonate
3% Sodium C_{12}—C_{15} alkylether sulphate (containing 3 moles of ethylene oxide)
4% Sodium salt of dipicolinic acid
4% Magnesium sulphate
10% Urea
2% Ethanol
50% Water
at a product concentration of 0.15%, the following results were obtained:

Water hardness (°FH)	Number of soil increments to destroy foam
5	40
10	39
24	41

These results show that in both soft and hard water a superior performance is obtained.

Example 6.

A composition comprising 27% sodium C_{11-13} alkylbenzene sulphonates, 40% dipicolinic acid, 10% magnesium sulphate and 23% sodium sulphate yielded at 0.15% product concentration the following results:

Water hardness (°FH)	Number of soil increments to destroy foam
4	36
24	36

Example 7.

The following compositions were compared, using the same method as in the foregoing examples. The compositions contained 27% sodium C_{11-13} alkylbenzenesulphonate, 3% sodium sulphate and

a) 0.2% N-(2-hydroxyethyl) ethylenediamine-N,N',N'-triacetate (trisodium salt) (Hydroxy-EDTA)

b) 0.2% Hydroxy-EDTA +1% magnesiumsulphate

c) 15% Hydroxy-EDTA +10% magnesiumsulphate.

Composition b) contained Hydroxy-EDTA and magnesiumsulphate in amounts as disclosed in Netherlands Patent Specification 7,404,849, and c) containing the same ingredients as in b), but in higher amounts, according to the invention.

These products were dosed in water of varying hardness to a product concentration of 0.15%, and subjected to the foam stability test as in the previous Examples. The following results were obtained:

Water hardness (°FH, Calcium)	Composition a	b	c
	Number of soil increments to destroy foam		
1	25	34	46
4	25	27	37
10	20	21	31
20	16	16	25

Example a) shows no improvement in hard water, example b) shows an improvement in soft water only and example c) shows improved performance at all levels of water hardness.

WHAT WE CLAIM IS:—

1. A hard surface cleaning composition for use in soft and hard water comprising an active detergent material, from 3—60% by weight of an organic sequestering agent having a pK value for calcium of at least 3, and a difference between the pK value for calcium and magnesium of at least 0.5, and from 0.5—30% by weight of an inorganic and/or organic magnesium salt with a solubility product of at least 5×10^{-5}.

2. A composition according to claim 1, in which the difference in pK values for calcium and magnesium is at least 1.0.

3. A composition according to claim 1, in which the pK value for calcium is not greater than 8.

4. A composition according to any one of claims 1—3, in which the organic sequestering agent is dipicolinic acid or its alkali metal, ammonium or substituted ammonium salt.

5. A composition according to claim 1, in which the magnesium salt is magnesium sulphate.

6. A composition according to any one of claims 1—5, comprising from 8—40% by weight of the organic sequestering agent and from 2—15% by weight of the magnesium salt.

7. A composition according to any one of claims 1—6, in which the active detergent material comprises at least 50% by weight of a calcium-sensitive anionic detergent having a solubility product of less than 6×10^{-11}.

8. A composition according to claim 7, in which the active detergent material comprises at least 50% by weight of a sodium (C_{10}—C_{18} alkyl)benzene sulphonate or a sodium C_{12}—C_{18} sec. alkane sulphonate.

9. A composition according to any of the preceding claims, substantially as described in any of the Examples 4, 5, 6 and 7c).

B. C. ROSCOE,
Chartered Patent Agent.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.